



# In situ synthesis of C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> heterojunction nanocomposite as highly visible light active photocatalyst originated from effective interfacial charge transfer



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## ABSTRACT

In this paper, a simple one-pot hydrothermal strategy was adopted to prepare C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> nanocomposite. Simultaneously, the photocatalytic performance of the C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> nanocomposite like tunable ratio was evaluated by the degradation of methyl orange (MO) under visible light irradiation. The prepared nanocomposite with the mass ratio of 27:8 (C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>(0.08)) possessed the highest photocatalytic activity, about 5.1, 3.8 and 2.3 times higher than that of C-TiO<sub>2</sub>, g-C<sub>3</sub>N<sub>4</sub>, and the Mixing sample, respectively. The excellent photocatalytic performance was attributed to the improvement of light harvesting and charge separation caused by construction of heterojunction. In addition, interfacial charge transfer through C–Ti bond and N–Ti bond also played a crucial role in inhibiting the recombination of electron-hole pairs and increasing the concentrations of holes and electrons, separately, which was confirmed by XPS analysis, photocurrent response experiment, electrochemical impedance spectroscopy measurements, PL spectra and Time-resolved PL spectra. Besides, the importance of active species during the reaction process was explored, and the generation of h<sup>+</sup>, O<sub>2</sub><sup>−</sup>, OH in the photocatalytic process was also demonstrated. Among this, O<sub>2</sub><sup>−</sup> played an important role. This finding about chemically bonded C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> nanocomposite provided a good guidance for the fabrication of new heterogeneous photocatalysts and facilitated their applications in environmental protection, water splitting and so on.

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## 1. Introduction

With improvements in science, photocatalysis technique has been considered to be a desired strategy for environmental remediation due to its low-cost, environmental benefit, nontoxicity and stability [1–4]. TiO<sub>2</sub> based nanomaterials have attracted considerable attention since Fujishima and Honda first reported the photoelectrochemical splitting of water on a TiO<sub>2</sub> semiconductor electrode in 1972 [5]. However, the problems including low efficiency in solar energy utilization and rapid recombination of photogenerated electron-hole pairs within TiO<sub>2</sub> hinder its practical application. Over the past few decades, various modification strategies have been developed to extend the photo-response range and

improve the photocatalytic performance [6–9]. In particular, coupling with narrow band-gap semiconductor is considered to be an effective method which can improve the separation efficiency of photogenerated electron-hole pairs in the photocatalytic process, such as BiOBr [10], CdS [11], Cu<sub>2</sub>O [12], Ag<sub>2</sub>O [13] and so on.

Recently, TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> nanocomposite has become a hotspot in the field of photocatalysis due to the enhancement of photocatalytic activity induced by the construction of heterojunction. Gu et al. prepared g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> hybrid, and enhancement of visible light photocatalytic activity over the hybrid was achieved [14]. Chen et al. investigated the visible-light photocatalytic performance of heterostructured g-C<sub>3</sub>N<sub>4</sub>/Ag/TiO<sub>2</sub> microspheres, and it showed significant photocatalytic activity [15]. The composite material comprising of doped TiO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub> has also attracted the researchers' attention, since it possesses the stronger visible light harvesting ability. Zhou et al. synthesized g-C<sub>3</sub>N<sub>4</sub>@N-TiO<sub>2</sub> heterojunction, and it exhibited enhanced photocatalytic performance for the selective photoreduction of CO<sub>2</sub> to CO [16]. Sridharan et al. found the improved photocatalytic activity in C and N co-doped

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$\text{TiO}_2/\text{g-C}_3\text{N}_4$  was owing to the formation of a synergistic heterojunction [17]. However, the effect of chemically bonded interface between  $\text{TiO}_2$  and  $\text{g-C}_3\text{N}_4$  on photocatalytic performance has been rarely reported.

In this paper, we report that a simple hydrothermal strategy is adopted to prepare  $\text{C-TiO}_2/\text{g-C}_3\text{N}_4$  nanocomposite with chemically bonded interface through C–Ti bond and NTi bond, which is confirmed by XPS analysis. Compared with the Mixing sample, the chemically bonded  $\text{C-TiO}_2/\text{g-C}_3\text{N}_4$  nanocomposite has higher separation efficiency of photogenerated electron-hole pairs, which is confirmed by the photocurrent response experiment, electrochemical impedance spectroscopy measurements, PL spectra and Time-resolved PL spectra. Hence, the chemically bonded  $\text{C-TiO}_2/\text{g-C}_3\text{N}_4$  nanocomposite exhibits an excellent visible light photocatalytic activity. Our work develop a simple method to prepare a kind of nanocomposites with effective interfacial charge transfer through chemical bond and provide theoretical basis for further studies.

## 2. Experimental

### 2.1. Materials

All chemicals applied in this experiment including tetra-*n*-butyl titanate (TTIP, 98%; Sinopharm Chemical Reagent Co., Ltd.), urea, ethylene glycol (EG) and ethanol were purchased and used without any further purification. High-purity deionized water was used throughout all experiments.

### 2.2. Synthesis of $\text{g-C}_3\text{N}_4$

The  $\text{g-C}_3\text{N}_4$  power was prepared by the thermal polycondensation of urea. In retail, 10 g of urea was put into a ceramic crucible with a cover, heated at 550 °C for 4 h with a temperature rise rate at 15 °C/min in a muffle furnace. After cooling to room temperature naturally, the resulting pale yellow products were collected and ground into powders.

### 2.3. Preparation of pure $\text{TiO}_2$ and $\text{C-TiO}_2$

The pure  $\text{TiO}_2$  and carbon-doped  $\text{TiO}_2$  ( $\text{C-TiO}_2$ ) were both prepared according to hydrothermal method. For the  $\text{C-TiO}_2$ , in a typical procedure, 1 mL TTIP was firstly dissolved in 40 mL EG at room temperature. Then, the above solution was added dropwise to the 40 mL deionized water under vigorous stirring for 30 min. Next, the final suspension solution was transferred into a 100 mL Teflon-lined autoclave, and maintained at 180 °C for 12 h. After cooling to ambient temperature naturally, the resulting product was centrifuged and rinsed with absolute ethanol and distilled water for several cycles to remove residual EG on the surface. The obtained precipitate was dried at 80 °C in a vacuum oven. The pure  $\text{TiO}_2$  was also obtained through the same process only without using EG.

### 2.4. Preparation of $\text{C-TiO}_2/\text{g-C}_3\text{N}_4$ nanocomposite

The  $\text{C-TiO}_2/\text{g-C}_3\text{N}_4$  was also synthesized by hydrothermal method. At first, a certain amount of  $\text{g-C}_3\text{N}_4$  was added to 40 mL distilled water under vigorous magnetic stirring for 1 h to form solution A. Likewise, 1 mL TTIP was dissolved in 40 mL EG at room temperature to form solution B. Then, solution B was added dropwise to solution A under vigorous stirring for 30 min. Afterwards, the mixed solution was transferred into a 100 mL Teflon-lined autoclave to react at 180 °C for 10 h. At last, the resulting product was centrifuged and washed with absolute ethanol and distilled water, and dried in a vacuum oven at 80 °C overnight to get the  $\text{C-TiO}_2/\text{g-C}_3\text{N}_4$  nanocomposite. By varying the dosage of  $\text{g-C}_3\text{N}_4$  at 0.02, 0.04,

0.06, 0.08 and 0.1 g, a series of  $\text{C-TiO}_2/\text{g-C}_3\text{N}_4$  nanocomposites were synthesized, labeled as  $\text{C-TiO}_2/\text{g-C}_3\text{N}_4(0.02)$ ,  $\text{C-TiO}_2/\text{g-C}_3\text{N}_4(0.04)$ ,  $\text{C-TiO}_2/\text{g-C}_3\text{N}_4(0.06)$ ,  $\text{C-TiO}_2/\text{g-C}_3\text{N}_4(0.08)$  and  $\text{C-TiO}_2/\text{g-C}_3\text{N}_4(0.1)$ , respectively. For comparison, a mixing sample with some mass ratios of  $\text{g-C}_3\text{N}_4$  to  $\text{C-TiO}_2$  to  $\text{C-TiO}_2/\text{g-C}_3\text{N}_4(0.08)$  was prepared by a simple mechanical mixing of  $\text{C-TiO}_2$  and  $\text{g-C}_3\text{N}_4$ , which was noted hereafter as “Mixing”.

## 2.5. Characterization

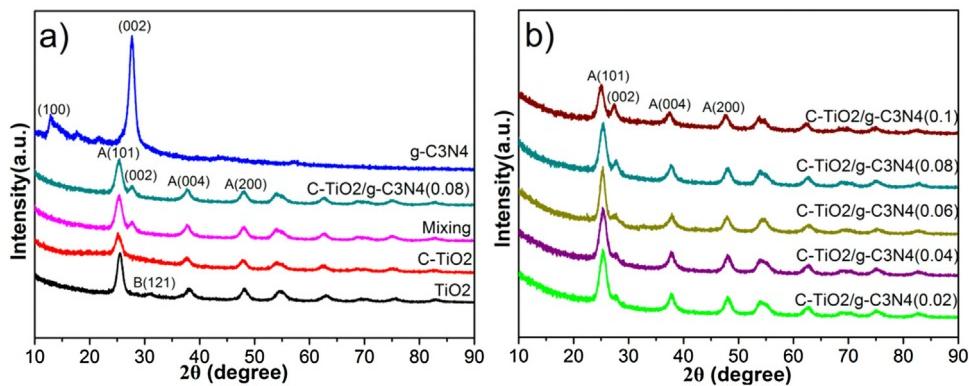
The crystal phases of all samples were characterized by X-ray diffraction (PANalytical B.V., Almelo, the Netherlands) with a Cu K $\alpha$  radiation, and their microstructures were observed by high-resolution transmission electron microscopy (HRTEM, FEI Tecnai G2 F30 field-emission TEM). Fourier transform infrared (FT-IR) spectra were recorded from a KBr disk on the FT-IR Bruker Tensor27. Chemical composition and valence band (VB) were detected by X-ray photoelectron spectroscopy (XPS) measurements in a VG Multilab2000 spectrometer. UV-vis diffuse reflectance spectroscopy (UV-vis DRS) absorption spectra were recorded at a Shimadzu U-3010 spectrometer using  $\text{BaSO}_4$  as a reference. Photoluminescence (PL) spectra of these powders were obtained on a Jasco FP-6500 with a laser excitation of 325 nm. Time-resolved PL decay (TRPL) spectroscopy was detected by a fluorescence spectrometer (F900) with an excitation wavelength of 375 nm. And the signals collected at excitation wavelength of 500 nm. ESR signals of  $\cdot\text{O}_2^-$  and  $\cdot\text{OH}$  with 5, 5-diethyl-1-pyrroline N-oxide (DMPO) were recorded with a Bruker A300-10/12 ESR spectrometer.

The electrochemical impedance spectroscopy measurements (EIS) were carried out on a Shanghai Chenhua CHI-660D electrochemical system by using a conventional three-electrode cell. The electrolyte solution was 0.1 M  $\text{Na}_2\text{SO}_4$ . The counter and the reference electrodes were platinum wire and saturated calomel electrode (SCE), respectively. The as-prepared photocatalyst powders were fixed to the film electrodes by the following method: First, 10 mg catalyst sample was mixed with 1 mL distilled water homogeneously (10 mg/mL). Then the solution was spin-coated onto an ITO glass electrode. At last, the electrode was dried naturally for 12 h and then dried at 120 °C for 5 h.

## 2.6. Photocatalytic activity test

The photocatalytic activities were evaluated by measuring the degradation of methyl orange (MO) in an aqueous solution under visible light irradiation ( $\lambda > 400 \text{ nm}$ ). In order to keep the temperature of MO solution maintained at room temperature, a liquid trap system with water circulation facility was used. A 300 W Xe lamp (CEL-HXF300) with a UV-cut off filter as visible light source was put 15 cm over the liquid trap system. Generally, 50 mg catalyst was well dispersed in 50 mL MO solution of 20 mg/L. Before photocatalytic experiments, the reaction suspensions were vigorously stirred for 30 min to ensure the absorption-desorption equilibrium of the MO on the catalyst surface. At a given time interval, 5 mL samples were taken from the suspensions and centrifuged. Then, the supernatant fluid was extracted immediately. The concentration of MO was analyzed by UV/vis spectroscopy. The degradation rate was calculated by  $C/C_0$ , where  $C$  was the concentration of MO in each time period, and  $C_0$  was the concentration of MO after dark adsorption. A blank control test without photocatalyst was performed for reference.

To identify the generated active species during the reaction process, ammonium oxalate (AO), 1, 4-benzoquinone (BQ) and 2-propanol (IPA) were used as the hole ( $\text{h}^+$ ) scavenger, superoxide radical ( $\cdot\text{O}_2^-$ ) scavenger and hydroxyl radical ( $\cdot\text{OH}$ ) scavenger, respectively. A proper amount of scavenger was added to the MO



**Fig. 1.** XRD patterns of all samples.

solution to probe the active species through variation of degradation rate.

### 3. Results and discussion

#### 3.1. XRD characterization

Fig. 1 shows the XRD patterns of all samples. From Fig. 1a, it is obvious that the pure TiO<sub>2</sub> sample can be indexed to the anatase (JCPDS file No. 21-1272) and brookite (JCPDS file No. 03-0380). However, the peak around 30° which is mainly indexed to brookite disappears and the main peaks shift to lower value in C-TiO<sub>2</sub>, it suggests that carbon atom has been incorporated into the TiO<sub>2</sub> successfully [18,19]. Meanwhile, it can be also found the crystal size of anatase decreases after carbon doping by comparing the (101) peak in Fig. 1a. The XRD pattern of g-C<sub>3</sub>N<sub>4</sub> clearly has two characteristic diffraction peaks at 13.05° (100) and 27.47° (002) which are attributed to the in-plane structure of tri-s-triazine units and the interlayer stacking of the conjugated aromatic groups, respectively [20,21]. For the C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>(0.08), the intensity of peak referred to g-C<sub>3</sub>N<sub>4</sub> decreases, it may be due to the relatively low amount. Similarly, the feature peaks of g-C<sub>3</sub>N<sub>4</sub> and C-TiO<sub>2</sub> phases are detectable in the Mixing sample, indicating that the phase composition of the Mixing sample is same to that of C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>(0.08). As displayed in Fig. 1b, the peaks of C-TiO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub> are clearly observed in all C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> nanocomposites, but the intensity of peak (002) increases as the increase of the mass of g-C<sub>3</sub>N<sub>4</sub>, this is supposed to be caused by the variation of mass ratios of g-C<sub>3</sub>N<sub>4</sub> to C-TiO<sub>2</sub>.

#### 3.2. TEM characterization

Fig. 2 shows the microstructures of as-prepared samples and elemental compositions of C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>(0.08). As shown in Fig. 2a, g-C<sub>3</sub>N<sub>4</sub> has a wrinkle sheet-like structure and the surface is not really smooth. Compared with TiO<sub>2</sub>, the grain size of the C-TiO<sub>2</sub> is relatively small, which is accord with the results of XRD. HRTEM images inserted in Fig. 2 show clear lattice fringes of TiO<sub>2</sub> and C-TiO<sub>2</sub>. The lattice of 0.35 nm corresponds to the (101) planes of the TiO<sub>2</sub> and C-TiO<sub>2</sub>. After adding g-C<sub>3</sub>N<sub>4</sub> in hydrothermal reaction, the C-TiO<sub>2</sub> particles are well dispersed on the g-C<sub>3</sub>N<sub>4</sub> in C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>(0.08), furthermore, the phase structure and particle size of C-TiO<sub>2</sub> both have no significant change. Similar to the C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>(0.08), C-TiO<sub>2</sub> particles are also located on g-C<sub>3</sub>N<sub>4</sub> nanosheet in the Mixing sample as shown in Fig. 2e, but the distribution of C-TiO<sub>2</sub> particles is non-uniform. Elemental compositions of the C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>(0.08) is analyzed by EDX spectra. As shown in Fig. 2f, the signals from C, N, Ti and O elements are detected.

Furthermore, a detailed chemical analysis was carried out using element mappings as shown in Fig. 3. It is clearly seen that the distribution of O element is consistent with its compositional element Ti, the C element is distributed across the whole surface, demonstrating that C element exists in the TiO<sub>2</sub>. Meanwhile, C element distribution is generally same with that of the compositional element N, which is assigned to the g-C<sub>3</sub>N<sub>4</sub> nanosheets. This result also indirectly indicates that C-TiO<sub>2</sub> particles are successfully incorporated with the g-C<sub>3</sub>N<sub>4</sub> nanosheets.

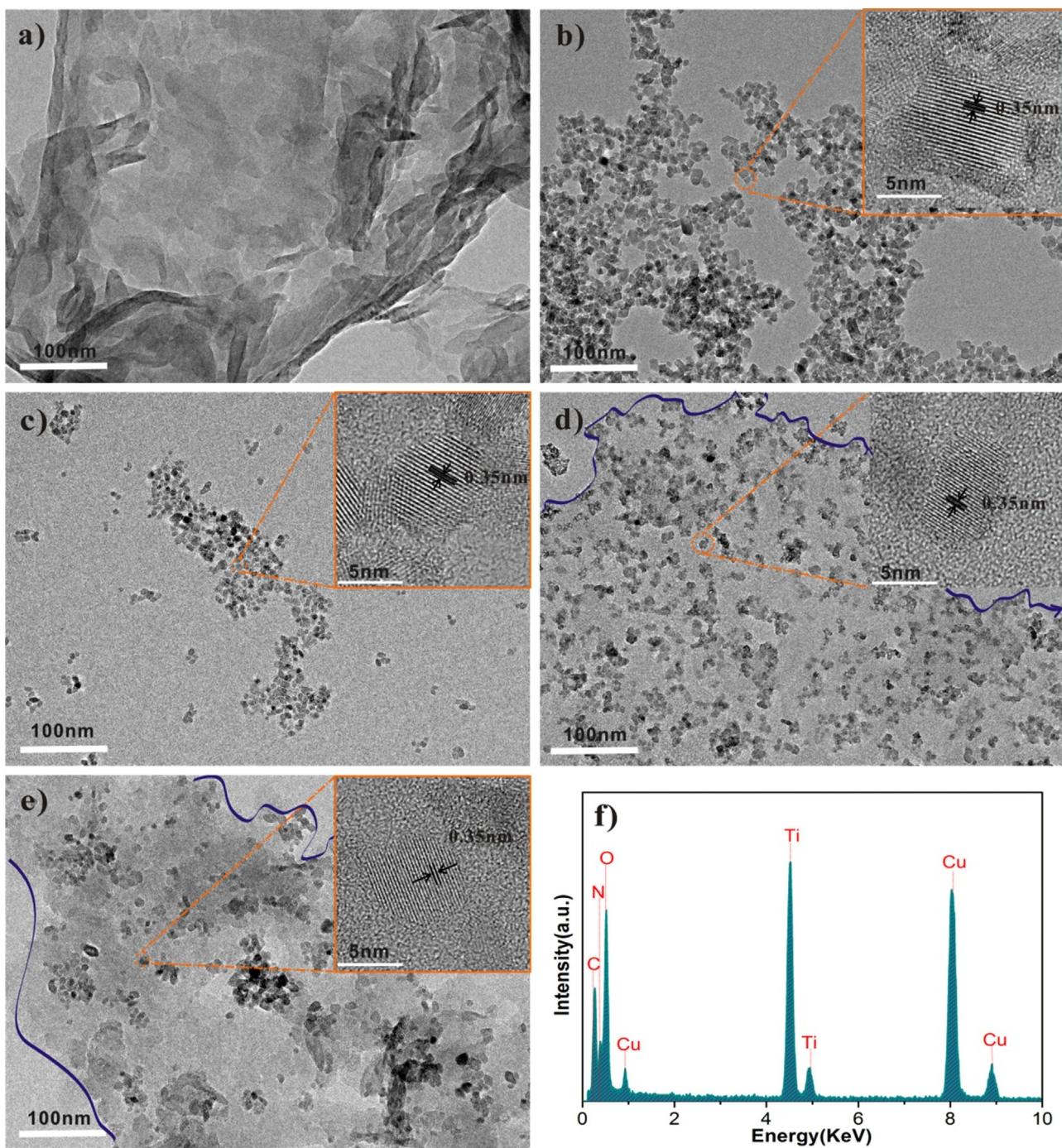
#### 3.3. FT-IR spectra

The local structures of all samples were investigated by FT-IR as shown in Fig. 4. For the pure TiO<sub>2</sub>, it can be seen that a band at 400–800 cm<sup>-1</sup> is clearly shown in the FT-IR spectrum of TiO<sub>2</sub>, which corresponds to the Ti—O—Ti stretching vibration [15,22,23]. Compared with TiO<sub>2</sub>, an additional absorption band near 1084 cm<sup>-1</sup> can be found in C-TiO<sub>2</sub> which is associated with C—O stretching, indicating that carbon atom has been incorporated into the lattice of TiO<sub>2</sub> and the formation of Ti—O—C group. As for g-C<sub>3</sub>N<sub>4</sub>, there are three characteristic bands: the absorption band at 1638 cm<sup>-1</sup> is attributed to C—N stretching vibration; the strong band at 1200–1600 cm<sup>-1</sup> is associated with the typical aromatic C—N stretching vibration; the band near 810 cm<sup>-1</sup> is related to out-of plane bending modes of C—N heterocycles [24–26]. For the Mixing sample and all C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> nanocomposites, all the FT-IR bands for C-TiO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub> are basically retained. This demonstrates that C-TiO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub> both exists in the Mixing sample and all C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> nanocomposites, which accords well with the result of XRD.

#### 3.4. Chemical compositions

To study the chemical composition and interaction between g-C<sub>3</sub>N<sub>4</sub> and C-TiO<sub>2</sub>, XPS analysis was utilized, as shown in Fig. 5.

Fig. 6a shows the high resolution XPS spectra of C 1s region. The binding energy of 284.8 eV is a typical peak position for adventitious carbon contamination adsorbed from the ambient environment, which cannot be eliminated. Furthermore, the deconvoluted peaks centered at the binding energy of 286.1 and 288.7 eV are attributed to the C—O and C=O oxygen-containing carbonaceous bands, severally [27,28]. C 1s spectra for C-TiO<sub>2</sub> is shown in Fig. 6b, the intensity of the peak at 286.1 eV increases obviously, indicating that the C—O bond forms in C-TiO<sub>2</sub>, that is, carbon atoms incorporate into interstitial positions of the TiO<sub>2</sub> lattice, which is coincident with the result of FT-IR [29]. For the C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>(0.08) nanocomposite, the peak at 288.1 eV can be distinguished for g-C<sub>3</sub>N<sub>4</sub>, which is assigned to sp<sup>2</sup>-hybridized carbon in the unit of (N)<sub>2</sub>—C=N [30]. In addition, an additional peak located at 282.5 eV is very close to the



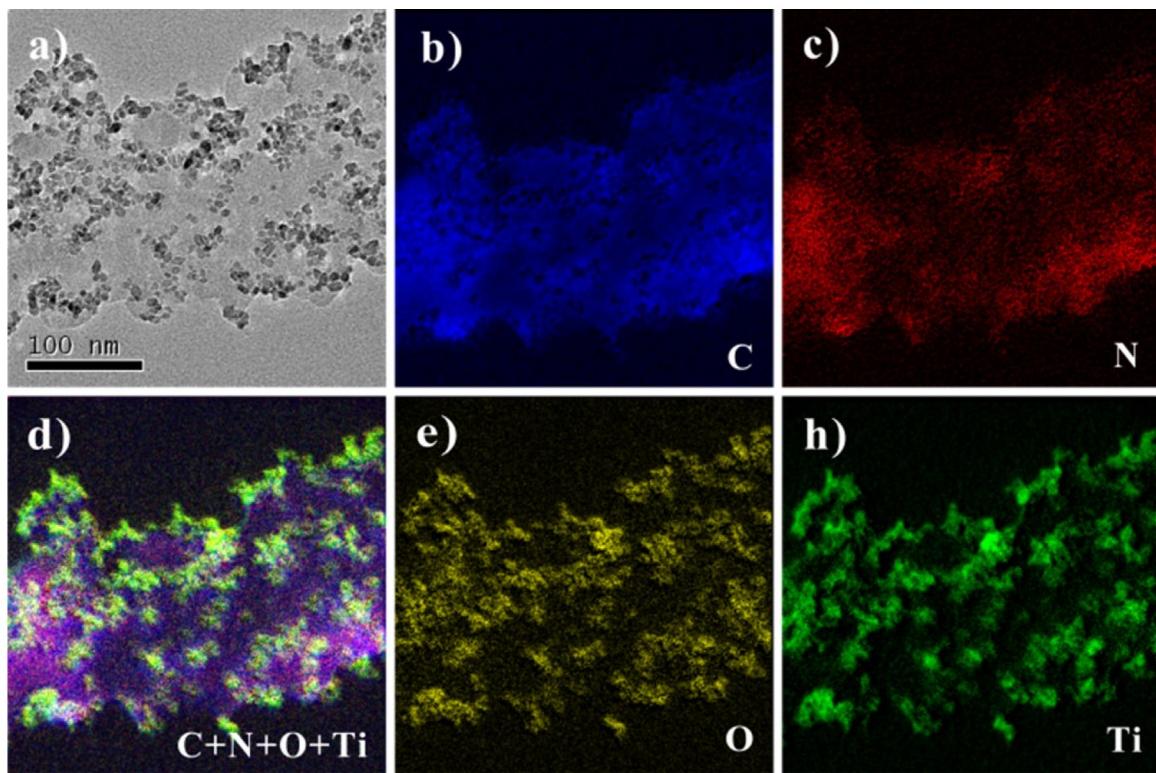
**Fig. 2.** TEM and HRTEM images of (a)  $\text{g-C}_3\text{N}_4$ , (b)  $\text{TiO}_2$ , (c)  $\text{C-TiO}_2$ , (d)  $\text{C-TiO}_2/\text{g-C}_3\text{N}_4(0.08)$ , (e) the Mixing sample and (f) EDX spectra of  $\text{C-TiO}_2/\text{g-C}_3\text{N}_4(0.08)$ .

C 1 s peak of  $\text{TiC}$ , which could be due to the formation of a chemical bond between the carbon atoms in  $\text{g-C}_3\text{N}_4$  and the titanium atoms in the lattice of  $\text{C-TiO}_2$  [28,31–33]. However, only the corresponding bonds for  $\text{C-TiO}_2$  and  $\text{g-C}_3\text{N}_4$  are retained in the Mixing sample as shown in Fig. 6d.

Fig. 7 shows the high resolution XPS spectra of N 1 s region for  $\text{C-TiO}_2/\text{g-C}_3\text{N}_4(0.08)$  (a) and the Mixing sample (b). For the  $\text{C-TiO}_2/\text{g-C}_3\text{N}_4(0.08)$  in Fig. 7a, there are three characteristic peaks corresponding to the  $\text{g-C}_3\text{N}_4$ , the peak at 398.5 eV is attributed to  $\text{C}-\text{N}=\text{C}$  group, while the other two peaks at 399.6 and 400.9 eV can be assigned to  $\text{N}-(\text{C})_3$  and  $\text{N}-\text{H}$  groups [34]. Meanwhile, an additional peak at 396.1 eV appears in  $\text{C-TiO}_2/\text{g-C}_3\text{N}_4(0.08)$ , which is usually assigned to the  $\text{N}-\text{Ti}$  bonding in this binding energy region

[35–37]. Combined with the results and analysis of C 1 s region, it suggests that there is an interaction between the  $\text{g-C}_3\text{N}_4$  and the  $\text{C-TiO}_2$  resulting from  $\text{C}-\text{Ti}$  bond and  $\text{N}-\text{Ti}$  bond. Thus, it indicates that the double-bond of  $\text{N}=\text{C}$  has been broken, nitrogen atom and carbon atom both bond with titanium atom, which results in the formation of  $\text{N}-\text{Ti}-\text{C}$  group. In Comparison with  $\text{C-TiO}_2/\text{g-C}_3\text{N}_4(0.08)$ , only three peaks attributed to  $\text{g-C}_3\text{N}_4$  exist in the Mixing sample as shown in the Fig. 7b.

As shown in Fig. 8, formation of the  $\text{C}-\text{Ti}$  bond and  $\text{N}-\text{Ti}$  bond in the  $\text{C-TiO}_2/\text{g-C}_3\text{N}_4(0.08)$  also can be further examined and confirmed by analysis of the  $\text{Ti} 2\text{p}$  core level of the XPS. For the pure  $\text{TiO}_2$ , the  $\text{Ti} 2\text{p}3/2$  and  $\text{Ti} 2\text{p}1/2$  centering at 458.8 eV and 464.5 eV are found respectively, which are assigned to  $\text{Ti}-\text{O}$  bond [29]. After



**Fig. 3.** TEM images of C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>(0.08): (a) TEM image; (b) C element map; (c) N element map; (d) multi-elemental image of C, O, N and Ti; (e) O element map; (h) Ti element map.

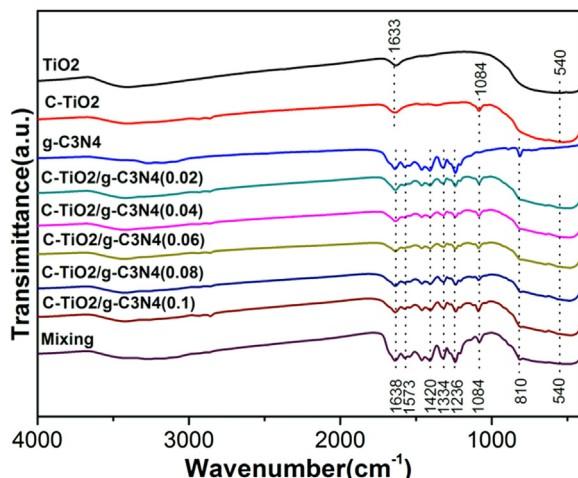
carbon doping, it is evident that only these two peaks which are also attributed to Ti–O bond appear, without other bonds exist. Hence, it is suggested that carbon atoms are doped into the interstitial positions of TiO<sub>2</sub> lattice. In Fig. 8c, in addition to the two characteristic peaks of TiO<sub>2</sub> at 458.8 (Ti 2p3/2) and 464.5 eV (Ti 2p1/2), another two peaks centered at 455.2 and 460.8 eV can be found and result from C–Ti bond [32,33], and the rest of peaks at 462.1 and 456.9 eV which are attributed to N–Ti bond [35]. But it is easy to observe that just two peaks at 458.8 and 464.5 eV can be assigned to Ti–O bond for the Mixing sample as shown in Fig. 8d. This demonstrates that the C–Ti bond and N–Ti bond are present in the C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>(0.08).

Combined with the above analysis, two additional bond (C–Ti bond and N–Ti bond) are formed in the C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>(0.08), it

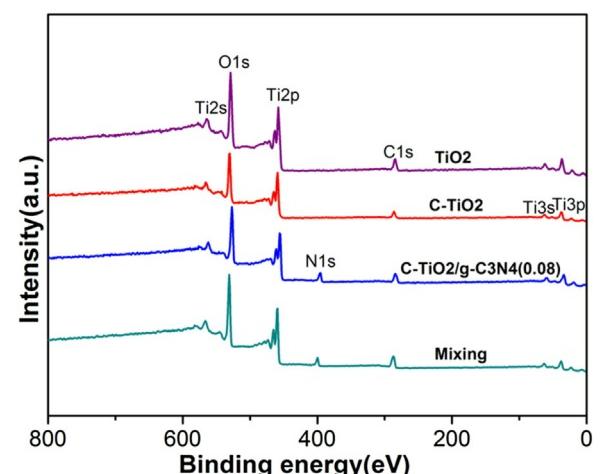
indicates that the C-TiO<sub>2</sub> nanoparticles are chemically bonding with the g-C<sub>3</sub>N<sub>4</sub> nanosheets in C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>(0.08).

### 3.5. UV-vis diffuse reflection spectra

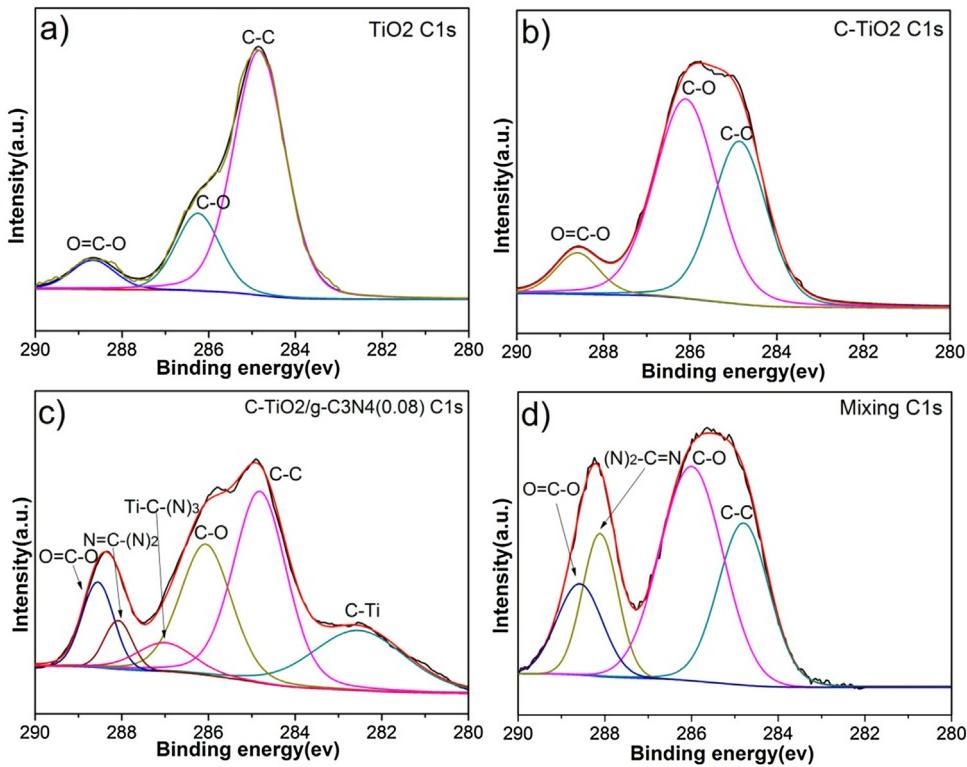
Fig. 9 shows the UV-vis spectra of all samples. It is obvious that the modified samples show significant red-shifts compared with pure TiO<sub>2</sub>. For C-TiO<sub>2</sub>, the existence of trailing is the characteristic of element doped TiO<sub>2</sub>, implying that carbon atoms have incorporated into the lattice of TiO<sub>2</sub>, which is consistent with the result of XPS. For g-C<sub>3</sub>N<sub>4</sub>, the absorption spectrum is cut off at 450 nm. The synergistic effect is apparently shown in all C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> nanocomposites, revealing that the advantage of single material still remains in every nanocomposite. It is obvious that the visible



**Fig. 4.** FT-IR patterns of all samples.



**Fig. 5.** XPS spectra: survey spectrum.



**Fig. 6.** C 1s XPS spectra of TiO<sub>2</sub> (a), C-TiO<sub>2</sub> (b), C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>(0.08) (c) and the Mixing sample (d).

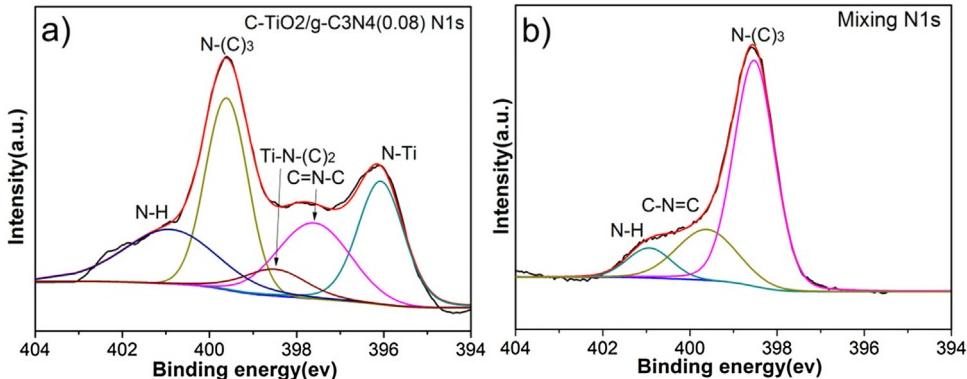
absorption ability of the Mixing sample is better than that of C-TiO<sub>2</sub>, but it is worse than that of C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>(0.08). As shown in Fig. 9b, C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>(0.08) exhibits the strongest visible light absorption from 400 nm to 700 nm and the trailing effect also exists.

To further research the band structure of C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> nanocomposite, the valance band (VB) and conduct band (CB) of TiO<sub>2</sub>, C-TiO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub> are determined by UV-vis DRS and VB-XPS. From Fig. 10a, it can be known that the corresponding band gaps of TiO<sub>2</sub>, C-TiO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub> are 3.18 eV, 2.73 eV and 2.65 eV, respectively. The band gap of the C-TiO<sub>2</sub> is estimated with a decrease of 0.45 eV, which is mainly attributed to C doping into the interstitial sites. Fig. 10b shows valence band XPS (VB-XPS) for the TiO<sub>2</sub>, C-TiO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub>. It indicates the VB of TiO<sub>2</sub> occurs at 2.74 eV. The VB edge of C-TiO<sub>2</sub> is at 2.29 eV, shifts toward negative energy than that of TiO<sub>2</sub>, meaning that the VB top of C-TiO<sub>2</sub> is indeed lifted up which is caused by the contribution of C 2p orbitals [38,39]. Therefore, their corresponding CB should be located at -0.45 eV. The VB of g-C<sub>3</sub>N<sub>4</sub> is revealed to be 1.71 eV, and the CB is calculated to be

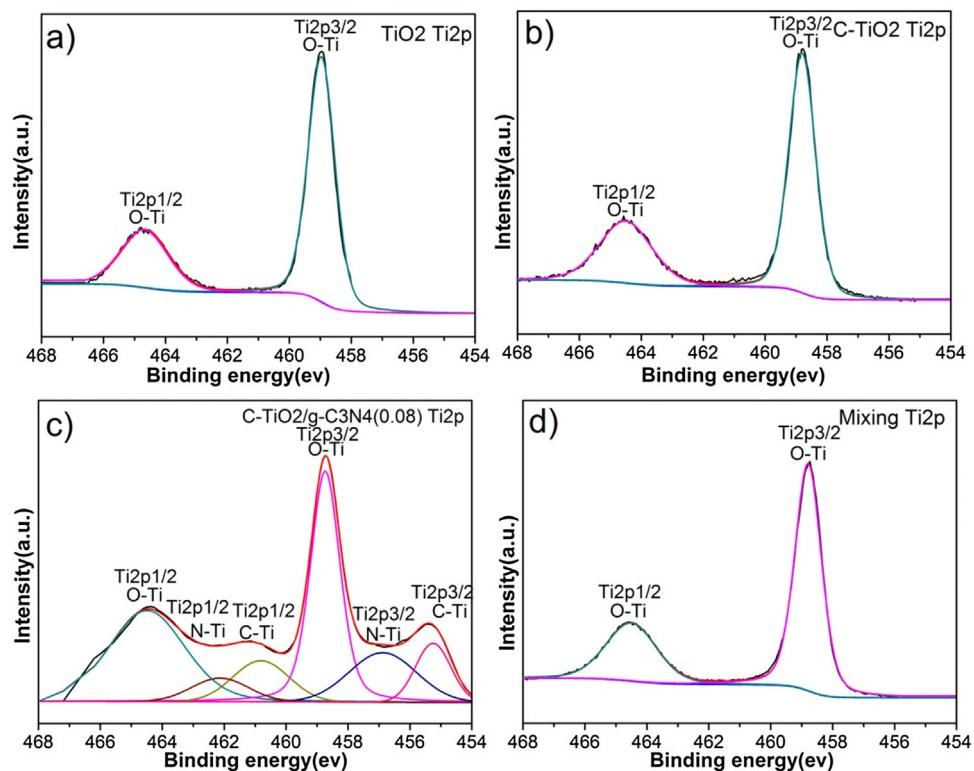
0.94 eV. So this heterojunction structure of C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> is benefit for the separation of electron-hole pair.

### 3.6. PL and time-resolved PL spectral analyses

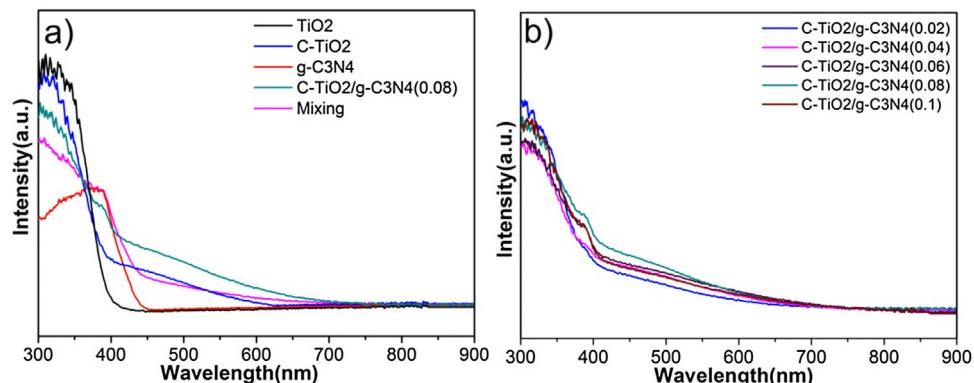
Fig. 11 shows the PL spectra of all samples. The samples are excited at 325 nm. The highest PL emission intensity is presented in the g-C<sub>3</sub>N<sub>4</sub> sample, indicating that the recombination of electron-hole pairs is the most severe. Obviously, the PL intensity decreases sharply after coupling with C-TiO<sub>2</sub>, as shown in Fig. 11. This is attributed to the formation of heterojunction between C-TiO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub>, which accelerates the electron-hole pair separation. Moreover, the PL intensity becomes weaker with the increase of g-C<sub>3</sub>N<sub>4</sub> in the C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> nanocomposite. Besides, it suddenly intensifies when the mass of g-C<sub>3</sub>N<sub>4</sub> is 0.1 g. Because g-C<sub>3</sub>N<sub>4</sub> dominates in the composition, the finite heterojunction limits the separation of charges. Similarity, the low addition of g-C<sub>3</sub>N<sub>4</sub> is unable to generate enough heterojunctions to aid charge separation. However,



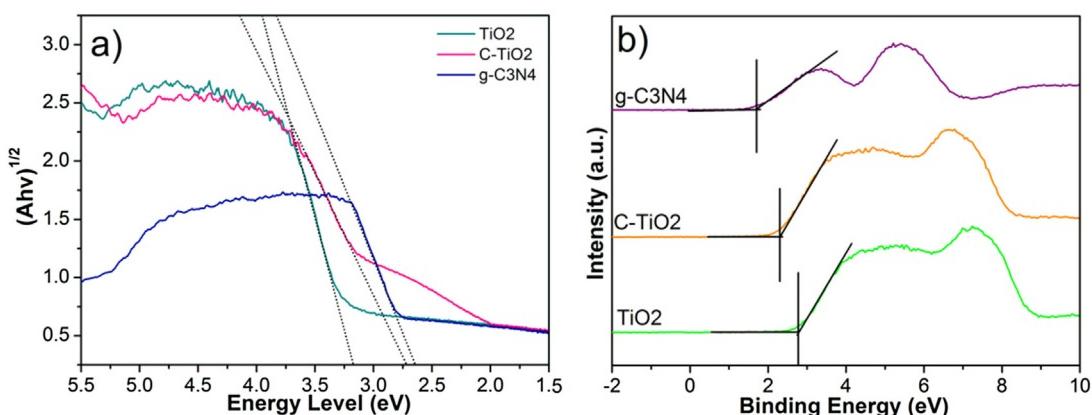
**Fig. 7.** N 1s high resolution XPS spectra of C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>(0.08) (a) and the Mixing sample (b).



**Fig. 8.** Ti 2p high resolution XPS spectra of  $\text{TiO}_2$  (a), C-TiO<sub>2</sub> (b), C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>(0.08) (c) and the Mixing sample (d).



**Fig. 9.** UV-vis DRS of all samples.



**Fig. 10.** Estimated band gaps (a); VB XPS spectra of  $\text{TiO}_2$ , C-TiO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub> (b).

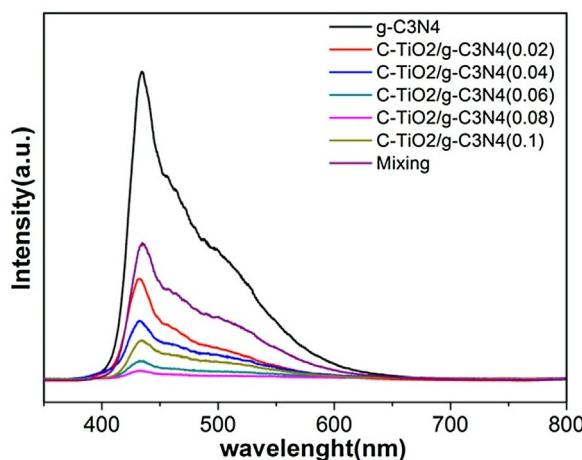


Fig. 11. PL spectra of all samples.

PL intensity of the Mixing sample is higher than those of all C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> nanocomposites; this could be caused by the poorer separation of electron-hole pairs.

To further depict the charge transfer of all samples, time-resolved PL spectra is shown in Fig. 12. Generally, the shorter lifetime is associated with the recombination of the electron-hole pairs, while the longer lifetime is attributed to fast separation of electron-hole pairs [40,41]. By multi-exponential fitting, values of the calculated decay time constant are shown in Table S1. For the decay curves of all samples, it can be seen that the lifetimes of the photogenerated charge carriers on all nanocomposites and the Mixing sample are slightly prolonged compared with each single component, which are consequently favorable for interfacial electron transfer after the construction of heterojunction. However, the C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>(0.08) has a longer lifetime compared with the Mixing sample, confirming that relatively better photogenerated carriers separation. This explains that the interfacial charge transfer through C—Ti bond and N—Ti bond plays an important role in facilitating the separation of electron-hole pairs. When the ratio of g-C<sub>3</sub>N<sub>4</sub> to C-TiO<sub>2</sub> increases gradually, the  $\tau$  increases first and decreases then, the result is accord with PL spectrum.

### 3.7. Photoelectrochemical measurements

To further investigate and understand the excitation and transfer of photogenerated charge carriers of all as-prepared samples, the photocurrent response (J-t) experiments shown in Fig. 13 were

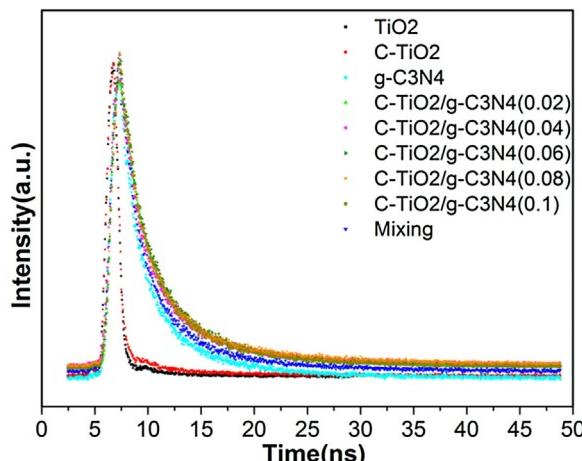
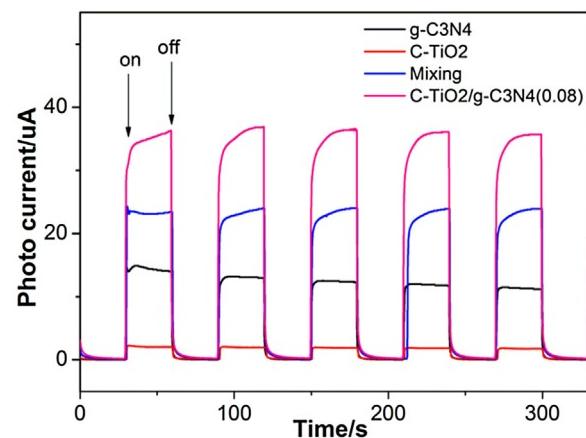


Fig. 12. Time-resolved PL spectra of all samples monitored at 500 nm.

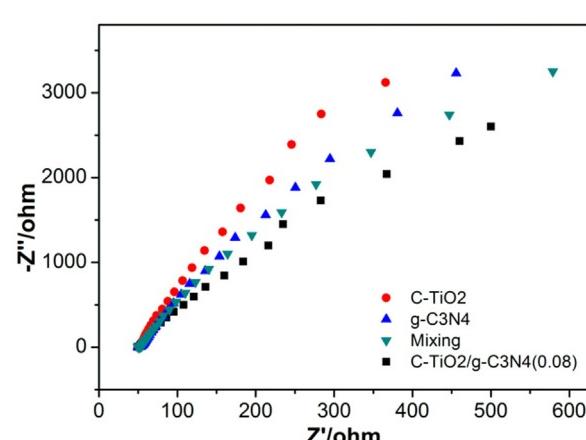
Fig. 13. Transient photocurrent responses of C-TiO<sub>2</sub>, g-C<sub>3</sub>N<sub>4</sub>, C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>(0.08) and the Mixing sample under visible light.

performed. It can be observed that all samples possess a relatively stable photocurrent response. The transient photocurrent density obtained over the C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>(0.08) is obviously higher than that of C-TiO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub> severally. Photocurrent density of the Mixing sample is also enhanced compared to that of each single component, but lower than that of the C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>(0.08). It can be seen clearly that C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>(0.08) possesses the highest photocurrent, indicating it has the most effective separation and the longest lifetime of the photogenerated electrons. And it is mainly due to the effective interfacial charge transfer through the chemical interactions and the synergistic effect of C-TiO<sub>2</sub> nanoparticles and g-C<sub>3</sub>N<sub>4</sub> nanosheets.

As shown in Fig. 14, EIS Nyquist analysis was performed to further investigate the interfacial electron transfer. Since the radius of each arc is related to the charge transfer process at the electrode/electrolyte interface, it suggests that the C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>(0.08) has a more effective separation of photogenerated electron-hole pairs and faster interfacial electron transfer. The result also indicates that chemical combination of C-TiO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub> is benefit to electron transfer, which agrees well with the result of the transient photocurrent responses.

### 3.8. Electron spin resonance spectra

To confirm the roles of •O<sub>2</sub><sup>−</sup> and •OH during photocatalytic process, ESR spectra of C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>(0.08) were performed using DMPO as radical trapper under visible light irradiation. As shown in

Fig. 14. Electrochemical impedance spectroscopy of C-TiO<sub>2</sub>, g-C<sub>3</sub>N<sub>4</sub>, C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>(0.08) and the Mixing sample.

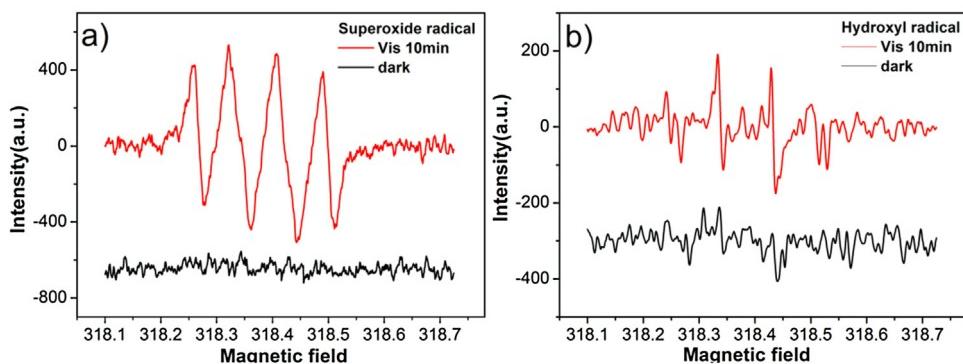


Fig. 15. ESR spectra of C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>(0.08) in aqueous solution before and after visible light irradiation: (a) DMPO-•O<sub>2</sub><sup>-</sup> and (b) DMPO-•OH.

Fig. 15a and b, no signals are detected in the dark. After 10 min visible light irradiation, the characteristic signals of the DMPO-•O<sub>2</sub><sup>-</sup> (Fig. 15a) and DMPO-•OH (Fig. 15b) are both observed obviously. The signal of •O<sub>2</sub><sup>-</sup> is much stronger than that of •OH under visible light. Because the holes transferred from the valence band (VB) of C-TiO<sub>2</sub> to the VB of g-C<sub>3</sub>N<sub>4</sub> once the heterojunction formed, however, VB of g-C<sub>3</sub>N<sub>4</sub> is -1.40 eV, cannot directly oxidize H<sub>2</sub>O or OH<sup>-</sup> into •OH radicals ( $E^{\theta}$  (H<sub>2</sub>O/•OH)= 2.40 V,  $E^{\theta}$  (OH<sup>-</sup>/•OH)= 1.99 V). So a small number of •OH radicals could be generated from the following reaction: •O<sub>2</sub><sup>-</sup> + e<sup>-</sup> + 2H<sup>+</sup> → H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub> + e<sup>-</sup> → •OH + OH<sup>-</sup>. Thus it can be seen that •O<sub>2</sub><sup>-</sup> is the main active species.

### 3.9. Photocatalytic activity

Fig. 16a displays the photocatalytic properties of all samples based on the degradation of MO under visible light irradiation. The results indicate that the pure TiO<sub>2</sub> has no catalytic activity under visible light irradiation, and the photocatalytic activities are greatly improved by the doping of carbon. Moreover, all C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> nanocomposites exhibit excellent photocatalytic activities

which are all higher than that of single component. When the mass ratio of C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> is 27:8 (C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>(0.08)), the photocatalytic activity is the best and the MO removal reaches about 98.6% after 1 h reaction. Compared with the C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>(0.08), the Mixing sample exhibits a poorer photocatalytic activity and the photodegradation rate of MO only reaches about 69.65%. In order to clarify the superiority of the C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>(0.08), the results of the comparison with the reported photocatalysts have been shown in Table S2. It indicates that the C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>(0.08) really exhibits great visible light photocatalysis performance.

The photocatalysis degradation follows the first-order kinetics. The kinetics can be expressed as follows:  $-\ln(C/C_0) = k_{app}t$ . Fig. 16b presents the linear relationship between  $\ln(C/C_0)$  and time, where  $C/C_0$  is the normalized as MO concentration, t is the reaction time, and k is the reaction rate constant ( $10^{-3} \text{ min}^{-1}$ ). Fig. 16c displays the reaction rate constants of all samples. The rate constant of C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>(0.08) is calculated to be  $0.0448 \text{ min}^{-1}$ , which is about 5.1, 3.8 and 2.3 times higher than that of C-TiO<sub>2</sub>, g-C<sub>3</sub>N<sub>4</sub> and the Mixing sample respectively. Therefore, it is convincing that the construction of a heterojunction structure with effective

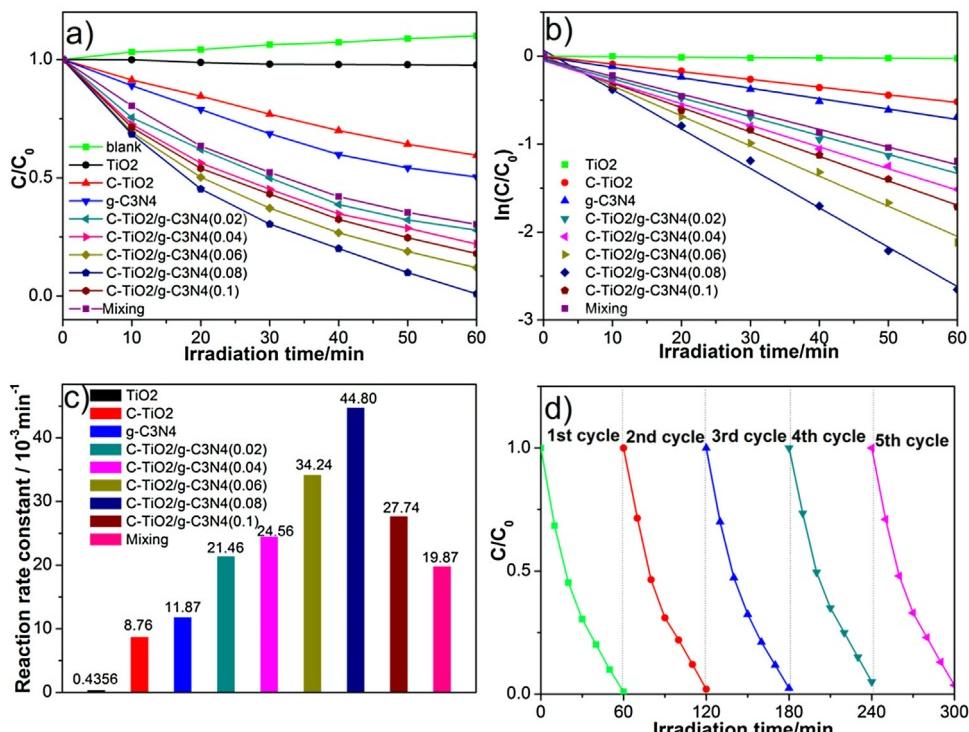


Fig. 16. (a) photodegradation rate of MO under visible light illuminated for 1 h on all samples; (b) kinetic curves for the photocatalytic degradation of all samples; (c) reaction rate constant of all samples; (d) stability study for the photocatalytic MO degradation by C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>(0.08).

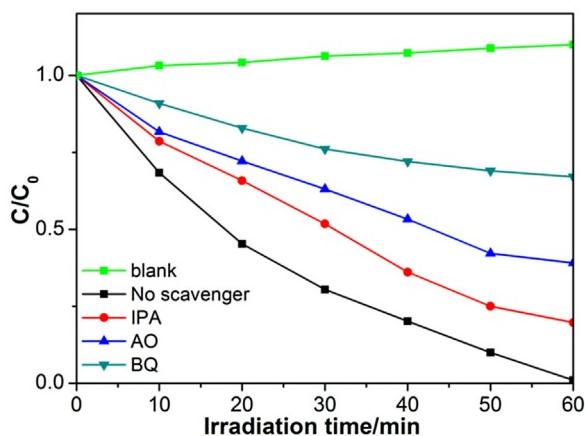


Fig. 17. Photodegradation rate of MO after different scavengers were added.

separation of electron-hole pairs through chemically bond connection as a visible light photocatalyst can enhance photocatalytic activities drastically.

For the practical application of photocatalysts, the stability of photocatalyst is one of the key issues. The by-products are always adsorbed on the surface-active position of the photocatalyst. The photocatalytic activity will decrease dramatically after a short period of exposure time. To evaluate the stability of as-prepared C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>(0.08), recycle experiments under same conditions were conducted. According results shown in Fig. 16d, the C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>(0.08) still exhibits superb catalytic performance in the fifth cycle.

To further explore the role of active species photogenerated in the reaction process, relevant scavengers are added to the MO solution through contrasting variation of degradation rate. As shown in Fig. 17, it clearly reveals that the degradation rate remarkably decreases after adding IPA, AO and BQ. And the degradation rate follows the order: No scavenger > IPA > AO > BQ. Therefore, it can be known that h<sup>+</sup>, O<sub>2</sub><sup>·-</sup>, OH as active species are generated in the photocatalytic reaction and O<sub>2</sub><sup>·-</sup> plays a significantly important role.

### 3.10. Mechanism discussion

Based on the above analysis and discussion, it can be concluded that chemically bonded interfacial contact between C-TiO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub> and the improvement of light harvesting are major factors for improving the photo-electrochemical performance and photocatalytic activity. As illustrated in Fig. 18, when the C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> nanocomposite is irradiated by visible light, electrons are excited from the VB to the CB of C-TiO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub>, leaving holes in the VB. Due to the CB of g-C<sub>3</sub>N<sub>4</sub> lies rather higher than C-TiO<sub>2</sub>, and the VB for g-C<sub>3</sub>N<sub>4</sub> is located at a higher position than C-TiO<sub>2</sub>, the excited electrons transfer from the CB of g-C<sub>3</sub>N<sub>4</sub> to the CB of C-TiO<sub>2</sub> while the holes migrate in the opposite direction. Moreover, the g-C<sub>3</sub>N<sub>4</sub> loading with C-TiO<sub>2</sub> with intimate chemically bonded (C-Ti bond and N-Ti bond) interfaces can be benefit for charge transport, hinder the recombination of electron-hole pairs and further increase the number of charge carrier in the reaction. Meanwhile, the C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> nanocomposite exhibits the strongest visible light absorption. And it is attributed to the narrowed gap which is caused by the migration of electrons and holes. So the chemically bonded C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> composite exhibits better photocatalytic activity.

On the basis of the ESR spectra and scavenger experiments, combined with the above mechanism analysis, the O<sub>2</sub><sup>·-</sup> is main role in the photocatalytic reaction generated from the reduction of

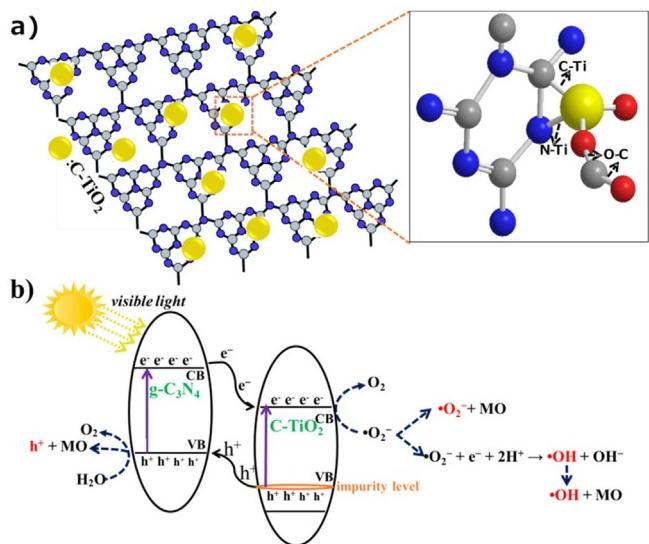
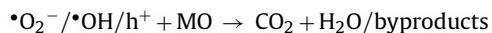
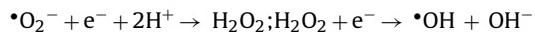
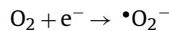
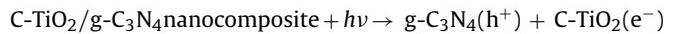


Fig. 18. Schematic illustrations for chemically bonded C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> nanocomposite (a) and photocatalytic process (b).

O<sub>2</sub> in the CB of C-TiO<sub>2</sub>. And the VB of g-C<sub>3</sub>N<sub>4</sub> is -1.40 eV, cannot directly oxidize H<sub>2</sub>O or OH<sup>-</sup> into •OH radicals, the •OH is produced from the further reaction of O<sub>2</sub><sup>·-</sup>, e<sup>-</sup> and 2H<sup>+</sup>. Photocatalytic process is shown in Fig. 18b and can be expressed by the following procedures.



### 4. Conclusions

In conclusion, C-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> nanocomposite with high photocatalytic activity was successfully synthesized by a facile hydrothermal method. And the optimum mass ratio of g-C<sub>3</sub>N<sub>4</sub> to C-TiO<sub>2</sub> was 27:8. TEM revealed that C-TiO<sub>2</sub> nanoparticles were well grown on the g-C<sub>3</sub>N<sub>4</sub> nanosheets surfaces. UV-vis spectra show that it exhibits the strongest visible light absorption. XPS indicated that the C-TiO<sub>2</sub> nanoparticles were chemically bonding with the g-C<sub>3</sub>N<sub>4</sub> nanosheets, which was confirmed by the formation of the C-Ti bond and N-Ti bond. This chemical bond combination structure was beneficial for the formation of effective heterojunction, which could result in a synergistic combination of C-TiO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub> that significantly decreased the recombination of electron-hole pairs and enhanced separation of photogenerated carrier. It was also demonstrated by the photocurrent response experiment, the electrochemical impedance spectroscopy measurements, PL spectra and Time-resolved PL spectra. Moreover, ESR spectra and scavengers experiments both revealed that O<sub>2</sub><sup>·-</sup> was the main role participating in the photocatalytic activity.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2016.09.052>.

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